

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
20 June 2002 (20.06.2002)

PCT

(10) International Publication Number
WO 02/48447 A1

(51) International Patent Classification⁷: D06L 1/04
(21) International Application Number: PCT/US01/26695
(22) International Filing Date: 24 August 2001 (24.08.2001)
(25) Filing Language: English
(26) Publication Language: English

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(30) Priority Data:
09/736,880 14 December 2000 (14.12.2000) US

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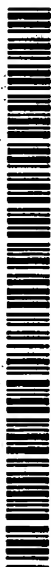
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(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 02/48447 A1

(54) Title: SILOXANE DRY CLEANING COMPOSITION AND PROCESS

(57) Abstract: A dry cleaning composition comprising a volatile siloxane and an aminofunctional siloxane and, optionally water or acid, and a method for dry cleaning comprising contacting an article with a composition comprising a volatile siloxane and an aminofunctional siloxane.

SILOXANE DRY CLEANING COMPOSITION AND PROCESS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims rights of priority from U.S. Provisional Patent Application Serial No. 60/188,244, filed March 10, 2000.

TECHNICAL FIELD

The present invention is directed to a dry cleaning composition, more specifically, to a siloxane fluid based composition, for use in dry cleaning and to a dry cleaning process using the composition.

BACKGROUND

Current dry cleaning technology uses perchloroethylene ("PERC") or petroleum-based materials as the cleaning solvent. PERC suffers from toxicity and odor issues. The petroleum-based products are not as effective as PERC in cleaning garments.

Cyclic siloxanes have been reported as spot cleaning solutions, see US 4,685,930, and as dry cleaning fluids in dry cleaning machines, see US 5,942,007. Other patents disclose the use of silicone soaps in petroleum solvents, see JP 09299687, and the use of silicone surfactants in super critical carbon dioxide solutions has been reported, see, for example, US 5,676,705 and Chem. Mark. Rep., 15 Dec 1997, 252(24), p. 15. Non-volatile silicone oils have also been used as the cleaning solvent requiring removal by a second washing with perfluoroalkane to remove the silicone oil, see JP 06327888.

Numerous other patents have issued in which siloxanes or organomodified silicones have been present as addenda in PERC or petroleum based dry cleaning solvents, see, for example, WO 9401510; US 4911853; US 4005231; US 4065258.

There is a continued interest in providing an additive or additives to enhance the cleaning ability of silicone based dry cleaning solvents.

SUMMARY OF THE INVENTION

In a first aspect, the present invention is directed to a dry cleaning composition, comprising a volatile siloxane and one or more aminofunctional siloxanes.

In a second aspect, the present invention is directed to a method for dry cleaning comprising contacting an article with a composition comprising a volatile siloxane and an aminofunctional siloxane.

The process of the present invention exhibits improved performance, such as for example, removal of water soluble stains from the article, for example a garment, being cleaned. The process of the present invention also exhibits improved performance for removal of soluble stains, including oil stains and grease stains.

DETAILED DESCRIPTION OF THE INVENTION

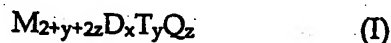
In a preferred embodiment, the composition comprises, based on 100 parts by weight ("pbw") of the composition, from greater than 90 pbw to 99.999 pbw, more preferably from 92 pbw to 99.9 pbw and even more preferably from 95 pbw to 99.5 pbw of the volatile siloxane and from 0.001 pbw to less than 10 pbw, more preferably from 0.01 pbw to 8 pbw and even more preferably from 0.1 pbw to 5 pbw of the aminofunctional siloxane or siloxanes. The volatile siloxane may be linear, branched, cyclic, or a combination thereof. The composition optionally further comprises water, preferably from 0.01 pbw to 15 pbw, more preferably from 0.1 pbw to less than 12 pbw and even more preferably from 0.2 pbw to 10 pbw of water. Preferably, the composition does not include siloxane resins or crosslinking

agents. The composition optionally further comprises acid in amounts sufficient to protonate the amino functionality of the aminofunctional silicone.

In a preferred embodiment, the water may be added as "free" water or may be delivered by an emulsion containing other components such as siloxanes, hydrocarbons, surfactants, or other suitable additives. If the water is delivered by an emulsion, the emulsion may be prepared by either homogenization of the components or by mechanically stirring the mixture.

Compounds suitable as the linear or branched, volatile siloxane solvent of the present invention are those containing a polysiloxane structure that includes from 2 to 20 silicon atoms. Preferably, the linear or branched, volatile siloxanes are relatively volatile materials, having, for example, a boiling of below about 300°C point at a pressure of 760 millimeters of mercury ("mm Hg").

In a preferred embodiment, the linear or branched, volatile siloxane comprises one or more compounds of the structural formula (I):



wherein:

M is $R^1_3SiO_{1/2}$;

D is $R^2R^3SiO_{2/2}$;

T is $R^4SiO_{3/2}$;

and Q is $SiO_{4/2}$

R^1 , R^2 , R^3 and R^4 are each independently a monovalent hydrocarbon radical; and

x and y are each integers, wherein $0 \leq x \leq 10$ and $0 \leq y \leq 10$ and $0 \leq z \leq 10$.

Suitable monovalent hydrocarbon groups include acyclic hydrocarbon radicals, monovalent alicyclic hydrocarbon radicals, monovalent and aromatic or fluoro containing hydrocarbon radicals. Preferred monovalent hydrocarbon radicals are monovalent alkyl radicals, monovalent aryl radicals and monovalent aralkyl radicals.

As used herein, the term "(C₁-C₆)alkyl" means a linear or branched alkyl group containing from 1 to 6 carbons per group, such as, for example, methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, pentyl, hexyl, preferably methyl.

As used herein, the term "aryl" means a monovalent unsaturated hydrocarbon ring system containing one or more aromatic or fluoro containing rings per group, which may optionally be substituted on the one or more aromatic or fluoro containing rings, preferably with one or more (C₁-C₆)alkyl groups and which, in the case of two or more rings, may be fused rings, including, for example, phenyl, 2,4,6-trimethylphenyl, 2-isopropylmethylphenyl, 1-pentalenyl, naphthyl, anthryl, preferably phenyl.

As used herein, the term "aralkyl" means an aryl derivative of an alkyl group, preferably a (C₂-C₆)alkyl group, wherein the alkyl portion of the aryl derivative may, optionally, be interrupted by an oxygen atom, such as, for example, phenylethyl, phenylpropyl, 2-(1-naphthyl)ethyl, preferably phenylpropyl, phenyloxypropyl, biphenyloxypropyl.

In a preferred embodiment, the monovalent hydrocarbon radical is a monovalent (C₁-C₆)alkyl radical, most preferably, methyl.

In a preferred embodiment, the linear or branched, volatile siloxane comprises one or more of, hexamethyldisiloxane, octamethyltrisiloxane,

decamethyltetrasiloxane, dodecamethylpentasiloxane, tetradecamethylhexasiloxane or hexadecamethylheptasiloxane or methyltris(trimethylsiloxy)silane. In a more highly preferred embodiment, the linear or branched, volatile siloxane of the present invention comprises

5 octamethyltrisiloxane, decamethyltetrasiloxane, or dodecamethylpentasiloxane or methyltris(trimethylsiloxy)silane. In a highly preferred embodiment, the siloxane component of the composition of the present invention consists essentially of decamethyltetrasiloxane.

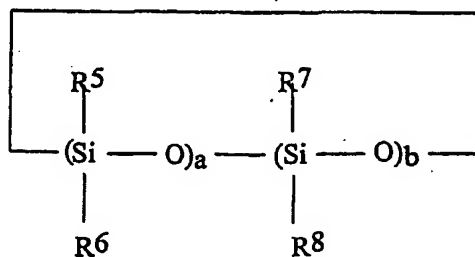
Suitable linear or branched volatile siloxanes are made by known

10 methods, such as, for example, hydrolysis and condensation of one or more of tetrachlorosilane, methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, or by isolation of the desired fraction of an equilibrate mixture of hexamethyldisiloxane and octamethylcyclotetrasiloxane or the like and are commercially available.

15 Compounds suitable as the cyclic siloxane component of the present invention are those containing a polysiloxane ring structure that includes from 2 to 20 silicon atoms in the ring. Preferably, the linear, volatile siloxanes and cyclic siloxanes are relatively volatile materials, having, for example, a boiling point of below about 300°C at a pressure of 760 millimeters of

20 mercury ("mm Hg").

In a preferred embodiment, the cyclic siloxane component comprises one or more compounds of the structural formula (II):



(II)

wherein:

R⁵, R⁶, R⁷ and R⁸ are each independently a monovalent hydrocarbon group;
and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq$
5 $(a + b) \leq 10$.

In a preferred embodiment, the cyclic siloxane comprises one or more
of, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane,
dodecamethylcyclohexasiloxane, tetradecamethylcycloheptasiloxane. In a
more highly preferred embodiment, the cyclic siloxane of the present
10 invention comprises octamethylcyclotetrasiloxane or
decamethylcyclopentasiloxane. In a highly preferred embodiment, the cyclic
siloxane component of the composition of the present invention consists
essentially of decamethylcyclopentasiloxane.

Suitable cyclic siloxanes are made by known methods, such as, for
15 example, hydrolysis and condensation of dimethyldichlorosilane and are
commercially available.

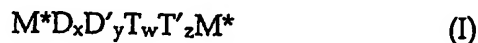
The aminofunctional silicone comprises structural units of the formula:



wherein at least one R²⁰ is $-(CHR^{24})_nNR^{25}R^{26}$ where R²⁴ is H or alkyl,
20 preferably (C₁-C₈)alkyl, R²⁵ is H or alkyl, preferably (C₁-C₄)alkyl, R²⁶ is H,
alkyl, preferably (C₁-C₈)alkyl, or $-(CHR^{27})_mNR^{28}R^{29}$ where R²⁷ is H or alkyl,
preferably (C₁-C₈)alkyl and R²⁸ and R²⁹ are each independently H or alkyl,
preferably (C₁-C₄)alkyl, n is from 2 to 16, and m is from 2 to 16; and $1 \leq f \leq 3$.

In a preferred embodiment, the aminofunctional silicone of the present
25 invention comprises one or more siloxanes selected from block or random

polymers and copolymers and terminally substituted aminofunctional siloxane polymers having the structural formula:



wherein M^* is $R^{21}R^{22}R^{23}SiO_{1/2}$, wherein each R^{21} , R^{22} and R^{23} is independently
 5 alkyl, preferably (C₁-C₈)alkyl, aryl, substituted alkyl or aryl, alkoxy, preferably (C₁-C₈)alkoxy, $-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl, preferably (C₁-C₈)alkyl, a is from 2 to 8 inclusive, b and c are each from 0 to 20 inclusive, or R^{20} , as previously defined;

D is $R^{14}_2SiO_{2/2}$, wherein each R^{14} is alkyl, preferably (C₁-C₈)alkyl or
 10 $-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl, preferably (C₁-C₈)alkyl, a is from 2 to 8 inclusive, b and c are each from 0 to 20 inclusive;

D' is $R^{10}R^{11}SiO_{2/2}$, wherein R^{10} is alkyl, preferably (C₁-C₈)alkyl, aryl, or
 $-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl, preferably (C₁-C₈)alkyl, a is from 2 to 8 inclusive, b and c are each from 0 to 20 inclusive,
 15 and R^{11} is R^{20} , as previously defined, or polyether, alkyl, aryl, or other functional side group;

T is $R^{12}SiO_{3/2}$, wherein R^{12} is alkyl or aryl, preferably (C₁-C₈)alkyl or
 $-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl, preferably (C₁-C₈)alkyl;

T' is $R^{13}SiO_{3/2}$, wherein R^{13} is alkyl, preferably (C₁-C₈)alkyl, aryl, or
 20 $-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl, preferably (C₁-C₈)alkyl, a is from 2 to 8 inclusive, b and c are each from 0 to 20 inclusive, and R^{11} is R^{20} , as previously defined, or polyether, alkyl, aryl, or other functional side group;

25 and w, x, y and z are integers such that $0 \leq w \leq 40$, $0 \leq x \leq 500$, $0 \leq y \leq 50$, $0 \leq z \leq 40$.

Compounds suitable as the aminofunctional silicone of the present invention include, but are not limited to, aminoethylaminopropyl linear graft copolymer, aminoethylaminopropyl branched graft copolymer, aminoethylaminopropyl terminal linear polymers, aminoethylaminoisobutyl
5 branched graft copolymers, aminoethylaminoisobutyl linear graft copolymers, aminoethylaminoisobutyl terminal linear polymers, aminopropyl graft linear copolymers, aminopropyl terminally substituted linear polymer, aminoethylaminopropyl linear graft terpolymer with ethylene oxide-
propylene oxide side chain, and the like.

10 In a preferred embodiment, the aminofunctional silicone of the present invention is an aminoalkyl substituted siloxane compound which may or may not be polymeric, wherein the aminoalkyl substituent is terminally substituted, substituted on a repeating unit, or both terminally substituted and substituted on a repeating unit, of a polymeric or copolymeric species,
15 such as an aminoalkyl terminally substituted linear siloxane, an aminoalkyl terminally substituted branched siloxane, a linear siloxane with aminoalkyl substitution on chain, a branched siloxane with an aminoalkyl substitution on chain, an aminoalkyl linear graft copolymer, an aminoalkyl branched graft copolymer, an aminoalkyl linear graft terpolymer, or an aminoalkyl branched
20 graft terpolymer.

In one preferred embodiment, each R^{21} , R^{22} , R^{23} and R^{10} is (C_1-C_8) alkyl, R^{11} is $(CH_2)_nNH(CH_2)_mNH_2$, and w and z are 0. In another preferred embodiment, each R^{21} , R^{22} , R^{23} , R^{10} and R^{12} is (C_1-C_8) alkyl, R^{11} is $(CH_2)_nNH(CH_2)_mNH_2$, R^{13} is a polyether, and w is 0. In another preferred
25 embodiment, each R^{21} , R^{22} , R^{23} , R^{10} and R^{15} is (C_1-C_8) alkyl, R^{11} is $(CH_2)_nNH(CH_2)_mNH_2$, and w is > 0 . In another preferred embodiment, each R^{21} , R^{22} , R^{10} and R^{14} is (C_1-C_8) alkyl, R^{23} is $(CH_2)NH_2$, w , y and z are 0, and x is from 2 to 100, preferably 2 to 10, preferably x is 2 or 10.

In a preferred embodiment, the dry cleaning composition of the present invention further comprises a minor amount, preferably, less than 50 pbw per 100 pbw of the composition, more preferably, less than 10 pbw per 100 pbw of the composition, of one or more non-siloxane fluids. Suitable non-
5 siloxane fluids include aqueous fluids, such as, for example, water, and organic fluids, for example, hydrocarbon fluids and halogenated hydrocarbon fluids.

In a preferred embodiment, the dry cleaning composition of the present invention further comprises a minor amount, preferably less than 10
10 pbw, more preferably less than 8 pbw, even more preferably less than 5 pbw per 100 pbw of the composition, of one or more surfactants. Suitable surfactants include organic surfactants such as anionic, nonionic, cationic and amphoteric surfactants, and silicone surfactants.

An article, such as for example, a textile or leather article, typically, a
15 garment, is dry cleaned by contacting the article with the composition of the present invention. In a preferred embodiment, the articles to be cleaned include textiles made from natural fibers, such as for example, cotton, wool, linen and hemp, from synthetic fibers, such as, for example, polyester fibers, polyamide fibers, polypropylene fibers and elastomeric fibers, from blends of
20 natural and synthetic fibers, from natural or synthetic leather or natural or synthetic fur.

The article and dry cleaning composition are then separated, by, for example, one or more of draining and centrifugation. In a preferred embodiment, separation of the article and dry cleaning composition is
25 followed by the application of heat, preferably, heating to a temperature of from 15°C to 120°C, preferably from 20°C to 100°C, or reduced pressure,

preferably, a pressure of from 1 mm Hg to 750 mm Hg, or by application of both heat and reduced pressure, to the article.

Testing for water soluble stain removal was accomplished using fabric swatches supplied by the International Fabricare Institute ("IFI") (Silver Spring, MD) that contained a water soluble dye. The color change of a swatch of this material was measured by a Minolta CR-300[®] Colorimeter using the Hunter Color Number difference calculations. The larger the change in Hunter Color Number (ΔE), the greater the dye removal and the more efficient the cleaning.

The following examples are to illustrate the invention and are not to be construed as limiting the claims.

EXAMPLES

Testing procedure: Circular swatches (from IFI) containing a water soluble dye were measured by the colorimeter, and the initial color values for L, a and b (as defined by the Hunter Color Numbers) were recorded. The fabric swatches were then placed in vials containing the cleaning composition of the present invention, and the vial was shaken for 10 minutes at ambient temperature. The fabric swatch was removed and allowed to drip dry for 2 to 5 seconds, then placed on absorbent toweling and allowed to air dry for 16 to 24 hours. A second reading of each fabric swatch was taken and the color difference (ΔE) was determined using the following formula:

$$\Delta E = [(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2]^{1/2}$$

This color difference represents the relative amount of cleaning, with the higher ΔE indicative of better cleaning performance.

Example 1 - Aminofunctional Siloxanes

A cleaning composition according to the present invention containing a cyclic siloxane (D₅) and one or more aminofunctional siloxanes was made.

Fabric swatches were cleaned using the above procedure, and the color difference was measured to determine the effectiveness of the cleaning

5 composition. A solution of cyclic siloxane (D₅) without a surfactant was used as a control.

Amino- functional Siloxane	Milli equiv. amine/g (approx.)	Aminofunctional Siloxane Structure
A	0.7	Aminoethylaminopropyl linear graft copolymer
B	0.55	Aminoethylaminopropyl branched graft copolymer
C	0.35	Aminoethylaminopropyl linear graft terpolymer with ethylene oxide-propylene oxide side chain
D	0.46	Aminoethylaminopropyl reactive branched graft copolymer
E	0.6	Aminoethylaminopropyl reactive linear graft copolymer
F	0.7	Aminoethylaminopropyl branched graft copolymer
G	5.1	Aminopropyl terminally substituted linear polymer
H	2.0	Aminopropyl terminally substituted linear polymer

Table 1 - Aminofunctional Siloxanes in D₅

Exp. No.	D ₅ (g)	Aminofunctional Siloxane	Amount (g)	ΔE
1	14.85	A	.15	1.7
2	14.25	A	.75	4.2
3	14.85	D	.15	1.9
4	14.25	D	.75	2.3
5	14.85	B	.15	1.6
6	14.25	B	.75	1.7
7	14.85	C	.15	3.5
8	14.25	C	.75	13.2
9	14.85	E	.15	2.0
10	14.25	E	.75	1.9
11	14.85	F	.15	1.8
12	14.25	F	.75	1.7
13	14.85	G	.15	6.3
14	14.25	G	.75	14.7
15	14.85	H	.15	2.9
16	14.25	H	.75	11.0
Control-1	15.00	-	-	1.9

Table 1 shows that some aminofunctional siloxanes enhance the cleaning and dye removal of the base cyclic siloxane (D₅) solvent.

Table 2 - Aminofunctional Siloxanes in D₅ with Water Added

Exp. No.	D ₅ (g)	Aminofunctional Siloxane	Amount (g)	Water (g)	ΔE
17	14.25	C	0.60	0.15	27.0
18	14.25	C	0.15	0.60	14.4
19	14.7	C	0.15	0.15	11.3
20	14.25	G	0.60	0.15	40.4
21	14.25	G	0.15	0.60	37.1
22	14.7	G	0.15	0.15	39.9
23	14.25	D	0.60	0.15	12.3
24	14.25	D	0.15	0.60	5.4
25	14.7	D	0.15	0.15	3.4
26	14.25	A	0.60	0.15	12.0
27	14.25	A	0.15	0.60	6.0
28	14.7	A	0.15	0.15	3.5
29	14.25	H	0.60	0.15	34.0
30	14.25	H	0.15	0.60	20.6
31	14.7	H	0.15	0.15	24.8
Control-1	15.00	-	-	-	1.9
Control-2	14.85	-	-	0.15	2.2
Control-3	14.40	-	-	0.60	9.5

Table 2 shows that the presence of water enhanced the cleaning action of the amino silicones.

Example 3 - Aminofunctional Siloxanes in D₅ with Acid Added

Exp.	D ₅ (g)	Aminofunctional Siloxane	Amt (g)	Water (g)	Acetic Acid	Delta E
32	14.85	C	0.15	-	5 micro L	2.65
33	14.25	C	0.75	-	20 micro L	5.93
34	14.25	C	0.6	0.15	15 micro L	6.60
35	14.25	C	0.15	0.6	5 micro L	30.31
36	14.7	C	0.15	0.15	5 micro L	6.55
37	14.85	G	0.15	-	45 micro L	23.36
38	14.25	G	0.75	-	225 micro L	30.73
39	14.25	G	0.6	0.15	180 micro L	30.69
40	14.25	G	0.15	0.6	45 micro L	31.98
41	14.7	G	0.15	0.15	45 micro L	37.69
42	14.85	H	0.15	-	20 micro L	23.41
43	14.25	H	0.75	-	90 micro L	30.71
44	14.25	H	0.6	0.15	75 micro L	33.22
45	14.25	H	0.15	0.6	20 micro L	33.20
46	14.7	H	0.15	0.15	20 micro L	32.26
47	14.85	A	0.15	-	10 micro L	6.14
48	14.25	A	0.75	-	35 micro L	4.66
49	14.25	A	0.6	0.15	30 micro L	4.70
50	14.25	A	0.15	0.6	10 micro L	3.01
51	14.7	A	0.15	0.15	10 micro L	4.15
Control 4	15.0	-	-	-	10 micro L	2.68
Control 5	14.85	-	-	0.15	10 micro L	2.11
Control 6	14.85	-	-	0.15	-	2.07

Table 3 shows that quaternized aminofunctional siloxanes also enhance cleaning of silicone solvents when compared to just the solvent, or solvent and water, acid or both.

Table 4 - Aminofunctional Emulsions

Exp.	D ₅ (g)	Emulsion	Amt (g)	% solids	Delta E
52	14.25	1	0.75	20	41.6
53	14.25	2	0.75	20	40.2
54	14.25	3	0.75	35	43.7
55	14.25	4	0.75	35	38.4

Emulsion	Components of Emulsion
1	2 alkyl aryl ethoxy alcohol surfactants, quaternary ammonium salt, and a curable amino siloxane
2	2 ethoxy alkyl alcohol surfactants, ethoxylated alcohol surfactant, and a commercially available aminofunctional emulsion (with A)
3	Quaternary ammonium salt, ethoxylated alcohol surfactant and commercially available curable trialkoxyaminosilane emulsion
4	Ethoxylated dialkyl ammonium salt, alkyl aryl ethoxy alcohol, and a curable trialkoxyaminosilane emulsion

The surfactants used in the emulsions are known in the art and are

commercially available as such trade names, for example, as Triton, Tergitol, Varisoft and the like.

Table 4 illustrates that emulsions of aminofunctional siloxanes and aminofunctional silanes, in conjunction with organic surfactants, are also effective at cleaning water soluble stains.

The present invention exhibits improved performance of dry cleaning agents for stain removal, particularly water soluble stains, through the addition of an aminofunctional silicone, and optionally water, acid or organic surfactants.

CLAIMS:

1. A dry cleaning composition, comprising a volatile cyclic, linear or branched siloxane, or combination thereof, and one or more aminofunctional siloxanes.

5 2. The composition of Claim 1, comprising from about 90 to about 99.999 parts by weight of the volatile siloxane and from about 0.001 to less than 10 parts by weight of the aminofunctional siloxane or siloxanes.

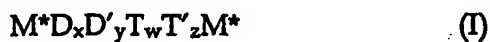
3. The composition of Claim 2, further comprising from about 0.01 to about 15 parts by weight of water.

10 4. The composition of Claim 1, wherein the aminofunctional siloxane comprises structural units of the formula:



wherein at least one R^{20} is $-(CHR^{24})_nNR^{25}R^{26}$ where R^{24} is H or alkyl, preferably (C_1-C_8) alkyl, R^{25} is H or alkyl, R^{26} is H, alkyl, or $-(CHR^{27})_mNR^{28}R^{29}$
 15 where R^{27} is H or alkyl, and R^{28} and R^{29} are each independently H or alkyl, n is from 2 to 16, and m is from 2 to 16; and $1 \leq f \leq 3$.

5. The composition of Claim 4, wherein the aminofunctional silicone comprises one or more siloxanes selected from block or random polymers and copolymers and terminally substituted aminofunctional siloxane polymers
 20 having the structural formula:



wherein M^* is $R^{21}R^{22}R^{23}SiO_{1/2}$, wherein each R^{21} , R^{22} and R^{23} is independently alkyl, aryl, substituted alkyl or aryl, alkoxy,

$-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl, a is from 2 to 8 inclusive, b and c are each from 0 to 20 inclusive, or R^{20} , as previously defined;

D is $R^{14}_2SiO_{2/2}$, wherein each R^{14} is alkyl or

5 $-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl, a is from 2 to 8 inclusive, b and c are each from 0 to 20 inclusive;

D' is $R^{10}R^{11}SiO_{2/2}$, wherein R^{10} is alkyl, aryl, or

10 $-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl, a is from 2 to 8 inclusive, b and c are each from 0 to 20 inclusive, and R^{11} is R^{20} , as previously defined, or polyether, alkyl, aryl, or other functional side group;

T is $R^{12}SiO_{3/2}$, wherein R^{12} is alkyl or aryl, or

$-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl;

T' is $R^{13}SiO_{3/2}$, wherein R^{13} is alkyl, aryl, or

15 $-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl, a is from 2 to 8 inclusive, b and c are each from 0 to 20 inclusive, and R^{11} is R^{20} , as previously defined, or polyether, alkyl, aryl, or other functional side group;

and w , x , y and z are integers such that $0 \leq w \leq 40$, $0 \leq x \leq 500$, $0 \leq y \leq 50$, $0 \leq z \leq 40$.

20 6. The composition of Claim 5, wherein each R^{21} , R^{22} , R^{23} and R^{10} is (C_1-C_8) alkyl, R^{11} is $(CH_2)_nNH(CH_2)_mNH_2$, and w and z are 0.

7. The composition of Claim 5, wherein each R^{21} , R^{22} , R^{23} , R^{10} and R^{12} is (C_1-C_8) alkyl, R^{11} is $(CH_2)_nNH(CH_2)_mNH_2$, R^{13} is a polyether, and w is 0.

8. The composition of Claim 5, wherein each R^{21} , R^{22} , R^{23} , R^{10} and R^{15} is (C_1-C_8) alkyl, R^{11} is $(CH_2)_nNH(CH_2)_mNH_2$, and w is > 0 .

9. The composition of Claim 5, wherein each R^{21} , R^{22} , R^{10} and R^{14} is (C_1-C_8) alkyl, R^{23} is $(CH_2)NH_2$, w, y and z are 0, and x is from 2 to 100.

10. The composition of Claim 9, wherein x is from 2 to 10, preferably x is 2 or 10.

5 11. The composition of Claim 10, wherein x is 2 or 10.

12. The composition of Claim 1, wherein the linear or branched,

volatile siloxane comprises one or more compounds of the structural formula:



wherein:

10 M is $R^1_3SiO_{1/2}$;

D is $R^2R^3SiO_{2/2}$;

T is $R^4SiO_{3/2}$;

and Q is $SiO_{4/2}$

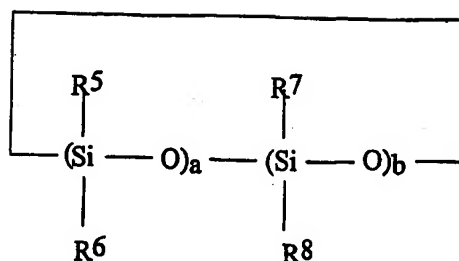
R^1 , R^2 , R^3 and R^4 are each independently a monovalent hydrocarbon radical;

15 and

x and y are each integers, wherein $0 \leq x \leq 10$ and $0 \leq y \leq 10$ and $0 \leq z \leq$

10.

13. The composition of Claim 1, wherein the cyclic siloxane component comprises one or more compounds of the structural formula:



wherein:

~~R⁵, R⁶, R⁷ and R⁸ are each independently a monovalent hydrocarbon group;~~
and

5 a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq (a + b) \leq 10$.

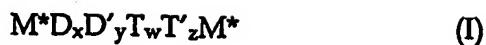
14. A method for dry cleaning an article, comprising contacting the article with a composition comprising a cyclic, linear or branched siloxane and one or more aminofunctional siloxanes.

10 15. The method of Claim 14, wherein the aminofunctional siloxane comprises structural units of the formula:



15 wherein at least one R²⁰ is $-(\text{CHR}^{24})_n\text{NR}^{25}\text{R}^{26}$ where R²⁴ is H or alkyl, preferably (C₁-C₈)alkyl, R²⁵ is H or alkyl, R²⁶ is H, alkyl, or $-(\text{CHR}^{27})_m\text{NR}^{28}\text{R}^{29}$ where R²⁷ is H or alkyl, and R²⁸ and R²⁹ are each independently H or alkyl, n is from 2 to 16, and m is from 2 to 16; and $1 \leq f \leq 3$.

20 16. The method of Claim 15, wherein the aminofunctional silicone comprises one or more siloxanes selected from block or random polymers and copolymers and terminally substituted aminofunctional siloxane polymers having the structural formula:



wherein M^* is $R^{21}R^{22}R^{23}SiO_{1/2}$, wherein each R^{21} , R^{22} and R^{23} is independently alkyl, aryl, substituted alkyl or aryl, alkoxy,

5 $-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl, a is from 2 to 8 inclusive, b and c are each from 0 to 20 inclusive, or R^{20} , as previously defined;

~~D is $R^{14}SiO_{2/2}$, wherein each R^{14} is alkyl or~~

~~$-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl, a is from 2 to 8 inclusive, b and c are each from 0 to 20 inclusive;~~

10 D' is $R^{10}R^{11}SiO_{2/2}$, wherein R^{10} is alkyl, aryl, or

$-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl, a is from 2 to 8 inclusive, b and c are each from 0 to 20 inclusive, and R^{11} is R^{20} , as previously defined, or polyether, alkyl, aryl, or other functional side group;

T is $R^{12}SiO_{3/2}$, wherein R^{12} is alkyl or aryl, or

15 $-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl;

T' is $R^{13}SiO_{3/2}$, wherein R^{13} is alkyl, aryl, or

$-(CH_2)_a(CH_2CH_2O)_b(CH_2CH(CH_3)O)_cR^{15}$, wherein R^{15} is H or alkyl, a is from 2 to 8 inclusive, b and c are each from 0 to 20 inclusive, and R^{11} is R^{20} , as previously defined, or polyether, alkyl, aryl, or other functional side group;

20 and w, x, y and z are integers such that $0 \leq w \leq 40$, $0 \leq x \leq 500$, $0 \leq y \leq 50$, $0 \leq z \leq 40$.

17. The method of Claim 16, wherein each R^{21} , R^{22} , R^{23} and R^{10} is $(C_1-C_8)alkyl$, R^{11} is $(CH_2)_nNH(CH_2)_mNH_2$, and w and z are 0.

18. The method of Claim 16, wherein each R^{21} , R^{22} , R^{23} , R^{10} and R^{12} is (C_1-C_8) alkyl, R^{11} is $(CH_2)_nNH(CH_2)_mNH_2$, R^{13} is a polyether, and w is 0.

19. The method of Claim 16, wherein each R^{21} , R^{22} , R^{23} , R^{10} and R^{15} is (C_1-C_8) alkyl, R^{11} is $(CH_2)_nNH(CH_2)_mNH_2$, and w is > 0 .

5 20. The composition of Claim 16, wherein each R^{21} , R^{22} , R^{10} and R^{14} is (C_1-C_8) alkyl, R^{23} is $(CH_2)NH_2$, w , y and z are 0, and x is from 2 to 100.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/26695

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D06L1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D06L C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 043 443 A (GEN ELECTRIC) 11 October 2000 (2000-10-11) page 4, line 41 - line 44; claims 8,9,11,12; example 3	1-20
Y	EP 0 375 028 A (PROCTER & GAMBLE) 27 June 1990 (1990-06-27) page 5, line 1 - line 20; claims 1,9,10	1-20

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Date of the actual completion of the international search

15 March 2002

Date of mailing of the international search report

27/03/2002

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/26695

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1043443	A	11-10-2000	US 6310029 B1	30-10-2001
			EP 1043443 A1	11-10-2000
			JP 2000313900 A	14-11-2000
			US 2001034912 A1	01-11-2001
EP 0375028	A	27-06-1990	US 4911853 A	27-03-1990
			AU 638440 B2	01-07-1993
			AU 4712889 A	28-06-1990
			BR 8906599 A	04-09-1990
			CA 2004163 A1	21-06-1990
			EP 0375028 A2	27-06-1990
			JP 2259159 A	19-10-1990
			KR 9700322 B1	08-01-1997
			MX 165880 B	08-12-1992

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